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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: M. Dahlbäck *et al.*

Application No.: 09/857,606	Group Art Unit: 1742
Filed: August 2, 2001	Examiner: H. Wilkins III

For: ZIRCONIUM BASED ALLOY AND COMPONENT IN A NUCLEAR ENERGY PLANT

SUBSTITUTE APPEAL BRIEF

Mail Stop Appeal Brief - Patents
Commissioner for Patents
PO Box 1450
Alexandria, Virginia 22313-1450

Sir:

This appeal is from the final Office Action mailed June 21, 2005 finally rejecting all of the pending claims, and also from the Examiner's Answer mailed February 14, 2006. In the Examiner's Answer, the Panel of Examiners (hereinafter "Examiner") withdrew several claim rejections presented in the final Office Action and added several new claim rejections that were not previously presented to the Appellants/Applicants. As a result, the Appellants submit this Substitute Appeal Brief, which includes additional evidence. Entry and consideration of the same is respectfully requested.

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REAL PARTY IN INTEREST

Westinghouse Electric Sweden AB, assignee of the instant application by virtue of the documents filed with the Assignment Division on January 25, 2005, is the real party in interest.

RELATED APPEALS AND INTERFERENCES

None.

STATUS OF CLAIMS

Claims 13, 22, 23, and 35-40 are pending, and claims 1-12, 14-21, and 24-34 are canceled. Claims 13, 22, 23, and 35-40 were rejected in the final Office Action dated June 21, 2005 and the Examiner's Answer dated February 14, 2006. The Appellants appeal the final rejection of claims 13, 22, 23, and 35-40.

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STATUS OF AMENDMENTS

No amendments were filed subsequent to final rejection. All amendments filed by the Appellant have been duly entered by the Examiner.

SUMMARY OF CLAIMED SUBJECT MATTER

The present invention as claimed relates to a cladding tube for nuclear fuel. The cladding tube is made of a zirconium-based alloy, suitable for use in a corrosive environment where it is subjected to increased radiation. *See, e.g.,* Written Description at page 1, lines 10-15[1]. The composition is formulated such that the alloy also exhibits excellent physical and mechanical properties. *Id.* at page 3, line 33 to page 4, line 4. To achieve these benefits, the alloy as now claimed contains: 0.65-1.6 weight percent niobium (Nb) to provide strength and to enhance corrosion resistance (*Id.* at page 7, lines 25-32; page 3, lines 7-9); 0.3-0.6 weight percent iron (Fe) to enhance corrosion resistance (*Id.* at page 7, lines 25-32; page 1, line 26 to page 2, line 3); 0.65-0.85 weight percent tin (Sn) to enhance the corrosion resistance (*Id.* at page 4, lines 13-30); the balance of the alloy being zirconium (Zr) (*Id.* at page 7, lines 25-32).

Of course, the alloy may contain impurities. *Id.* at page 9, lines 17-18. Small amounts of silicon and oxygen may be present. *Id.* at page 9, lines 18-21. The exact amount of these impurities will necessarily vary due to manufacturing. The alloy may thus include up to 1600 ppm oxygen and up to 120 ppm silicon. Typically expected amounts of silicon are 50-120 ppm, and typically expected amounts of oxygen are 500-1600 ppm. *Id.* at page 9, lines 15-30.

The cladding tube is designed for use in a nuclear power plant. *Id.* at page 6, lines 5-6. The inventive alloy is ideal for such a component due to its ability to withstand heightened corrosion effects of fast neutron radiation that is present in such an environment, especially around the reactor core. *Id.* at page 6, lines 5-31.

According to one embodiment, at least a part of the cladding tube inner circumference has a layer of a material which is more ductile than the inventive alloy. *Id.* at page 6, lines 33-

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[1] Citations are to the PCT publication (WO 00/36170).

36. This may help ensure that the cladding tube is less sensitive to the direct contact with the fuel and that the risk of cracking is reduced. *Id.* at page 6, line 36 to page 7, line 7. To this end, the ductile layer include a zirconium-based alloy with a total content of alloying materials which does not exceed 0.5 percentage by weight. *Id.* at page 7, lines 7-9.

GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

The grounds of rejection to be reviewed on appeal are:

1.   Whether claims 13, 22, and 23 are unpatentable under 35 U.S.C. § 112, first paragraph.

2.   Whether claims 13 and 35 are unpatentable under 35 U.S.C. § 102 over U.S. Patent No. 5,023,048 to Mardon *et al.* (Mardon) as supported by U.S. Patent Nos. 5,790,623 to Van Swam (Van Swam) and 5,254,308 to Garde *et al.* (Garde '308).

3.   Whether claim 38 is unpatentable under 35 U.S.C. § 103 over Mardon modified by U.S. Patent No. 5,211,774 to Garde *et al.* (Garde '774).

4.   Whether claims 22, 23, 36, and 37 are unpatentable under 35 U.S.C. § 103 over Mardon modified by Van Swam.

5.   Whether claims 39 and 40 are unpatentable under 35 U.S.C. § 103 over Mardon modified by Garde '774 and Van Swam.

ARGUMENT

Rejections under 35 U.S.C. § 112, first paragraph

The Examiner rejected claims 13, 22, and 23, alleging that the claims contain subject matter that was not adequately described in the specification. Specifically, the Examiner stated that "[t]he specification only provides support for the range of O being 500-1600 ppm."

Claim 13 recites "... the alloy having a quality and impurity level, including up to 1600 ppm O ...." This recitation is supported in the specification. As expressly stated, "small amounts of Si and O *may* exist in the alloy." Written Description at page 9, lines 20-21 (emphasis added). Clearly, this means that small amounts of oxygen may exist in the alloy or there may be no oxygen in the alloy. The Appellants expressly state a range of oxygen that typically may be expected in the alloy - 500-1600 ppm. *Id.* at page 9, lines 29-30. This, however, is not the only amount of oxygen that may be present. As previously established, *small amounts* of Si and O may exist in the alloy. If 500-1600 ppm qualifies as a "small amount" of oxygen, surely 0-500 ppm must also qualify as a small amount of oxygen. Furthermore, because the exemplary range of oxygen is described as being *typical*, it cannot be read to be the *only* range possible. *See Id.* at page 9, lines 21-22. Finally, it is nonsensical to think that 500-1600 ppm is the only amount of oxygen qualifying as an impurity level. *See Id.* at page 9, lines 17-18, 20-21.

Thus, "up to 1600 ppm O" is disclosed and supported in the written description, and the Examiner's rejections under 35 U.S.C. § 112, first paragraph, of claims 13, 22, and 23 are improper and must be withdrawn.

Rejection of Claims 13 and 35 under 35 U.S.C. § 102 over Mardon as supported by Van Swam and Garde '308

Mardon appears to disclose a so-called duplex tube. Such a duplex tube comprises a main tubular element provided with an outer surface layer. It is clear from the abstract that this layer only constitutes 10-25% of the total thickness of the wall. The concept "duplex tube" is also explained in, for example, column 1, lines 49-62. Mardon thus suggests a particular duplex tube. The main portion of this tube is made of a zirconium alloy of conventional type (see, for example, column 2 lines 55-68). These conventional alloys are very different from the inventive alloy of the present invention. Consequently, Mardon does not teach the present invention.

In contrast to Mardon, the present invention discloses and claims a cladding tube *made of* the defined alloy. *Cf.* Written Description at page 6, lines 28-29; page 7, lines 22-23. According to one embodiment, the cladding tube may be provided with an inner protective layer. As is known in art, such a layer is often called a liner, and such a layer is rather thin compared to the thickness of the alloy from which the cladding tube is made. *See, for example,* Van Swam at column 2, lines 22-42. It is thus clear from the wording of the instant claims, in view of the description and in accordance with how the terms are used in the art, that the present invention claims a cladding tube for which the main part (or the entirety) is formed by the novel alloy defined in the independent claims. For this reason alone it is clear that the present invention is new and inventive and patentable over Mardon.

Furthermore, Mardon does not teach that its thin outer layer should constitute the base material for the tubular element. On the contrary, as explained above, this layer is only used as an external protective layer. The composition of the alloy in this protective layer is given in examples 1-3 in column 3. Example 1 defines an Fe range that does not at all overlap with the Fe range of the alloy of present invention. Example 3 includes V but not Nb, and is therefore not

in accordance with the alloy of the present invention. Example 2 includes an Fe content that is within the range defined in the present independent claims. However, example 2 teaches a lower Sn content, that only coincides with the range defined in the present independent claims at the exact value 0.65. Furthermore, example 2 in the cited document teaches a Nb content that is essentially lower than according to the present invention. The Nb content only coincides with the range defined in the present independent claims at the exact value 0.65. Furthermore, Mardon example 2 only mentions ranges for each of the elements of the alloy; it does not teach any concrete example of how to choose the exact amounts of the different elements. A person skilled in the art, who would like to fabricate the tubular element according to Mardon, has, by necessity, to choose some particular values for the different alloying elements. There is no indication in Mardon that a person skilled in the art would choose exactly the upper limit (0.65) for Sn and at the same time select the very highest upper limit for the Nb content (0.65). This means that Mardon does not suggest the alloy defined in the independent claims of the present application. On the contrary, even the alloy according to Mardon example 2 teaches away from the alloy defined in the present independent claims, since Mardon teaches a lower range for the Sn content and a lower range for the Nb content. Mardon therefore does not suggest an alloy according to the present invention even in connection with the outer protective layer described therein. Moreover, Mardon does not even suggest such an alloy for the main portion of the tubular element.

The Examiner has alleged that the Appellants are attempting to ascribe a novel meaning to the term *cladding tube*, and further states that "[a] cladding tube is any tube shaped object which surrounds a cylindrical object." June 21, 2005 final Office Action at section 8b. The Appellants respectfully traverse the Examiner's statements. The examiner equates the thinner

protective surface layer in the duplex tube of Mardon with a cladding tube. This external layer itself is not a cladding tube as the term is known or used in the art. Instead, it constitutes just a thinner protective surface layer. *See* Mardon at column 1, lines 49-63; column 2, lines 21-27. The main part of the tube according to Mardon is made of a conventional alloy. Such an alloy is very different from the alloy of which the cladding tube according to the present invention is made. Consequently, Mardon does not disclose a cladding tube as defined in the claims. Furthermore, as explained above, not even the thin external layer with which the tube according to Mardon is provided defines the same alloy as the alloy of which the cladding tube according to the present invention is made.

Thus, the Examiner's rejections of claims 13 and 35 are improper and must be withdrawn.

Rejection of Claim 38 under 35 U.S.C. § 103 over Mardon modified by Garde '774

The statements made above regarding the Examiner's improper use of the Mardon reference to claims 13 and 35 are equally applicable to claim 38, and are thus incorporated herein.

Concerning claim 38, the Examiner argues that the subject matter of this claim is obvious in view of Mardon in combination with Garde '774. June 21, 2005 final Office Action at section 6; February 14, 2006 Examiner's Answer at page 4. In this context, the Examiner still refers to the outer surface layer in Mardon. As explained above, the alloy in this layer is not relevant to the present invention. Nevertheless, the Examiner argues that it would be obvious to add 50-120 ppm Si to the alloy in this outer duplex layer of Mardon in view of Garde '774. *Id.*

Garde '774 teaches a particular alloy that is said to have advantageous properties concerning corrosion resistance, ductility, and reduced hydrogen absorption. *See* Garde '774 at

the Abstract. Garde '774 explicitly teaches that the niobium content should be at the most 0.6%, typically 0.3%. *See, for example,* column 3, lines 31-39. The amount of niobium is thus clearly lower than in the alloy according to the present invention.

If a person skilled in the art would at all be interested in combining the teaching of Mardon with that of Garde '774, this person would make sure that the niobium content is lower than 0.6% in accordance with the teaching of Garde '774. *See Id.* The person skilled in the art would therefore not arrive at an alloy as defined in the pending claim 38. On the contrary, Garde '774 clearly supports the non-obviousness of the present invention, since this document teaches that a person skilled in the art should *not* select the highest value of niobium in the range specified in Mardon.

Moreover, Garde '774 teaches that the alloy should include 0.1-0.4% Cr. *See, for example,* Garde '774 column 3, lines 24-29; Table 1. However, Mardon explains that the outer layer shall not contain any chromium at all. *See, for example,* Mardon at the table in column 3; column 3, lines 21-22. Consequently, it would not be obvious to apply the teaching of Garde '774 to Mardon. Because Garde '774 concerns a completely different alloy than the alloy in the outer layer of Mardon, it would not be obvious to select one individual element (silicon) out of context in Garde '774 and to use this amount out of context in the outer layer of Mardon. In response, the Examiner attempts to overcome the Appellants' arguments by stating that "[t]he function of Si operates independent of any other element in the alloy (in other words, it does not act in conjunction with any other element.)" February 14, 2006 Examiner's Answer at page 10. The Examiner, however, offers no support for such statement. Contrary to the Examiner's unsubstantiated assertion, the different elements in alloys interact with each other in a very complicated manner to give the alloy certain properties. It is very difficult to predict the

property of a new alloy on the basis of the addition of a newly included element. The Examiner is thus completely wrong in asserting that the function of silicon operates independent of any other element in the alloy. As already explained, Garde '774 concerns an alloy with a completely different composition than the composition of the outer layer in Mardon. It is therefore not obvious to single out silicon in the alloy according to Garde '774 and apply this element to the outer layer in Mardon. Further to this point, attention is directed to a new declaration of Magnus Limbäck, attached here as Exhibit C.

It should also be noted that Garde '774 is completely based on the idea of modifying the contents of alloying elements in traditional alloys such as Zircaloy-4. *See, for example,* Garde '774 at column 2, lines 52-62. If the teaching of Garde '774 were to be combined with the teaching of Mardon, it would therefore be in order to modify the alloy of the base material of Mardon, as this material typically can be Zircaloy-4. *See, for example,* Mardon at column 2, lines 55-68. However, such a combination would not lead to the present invention.

Furthermore, the Examiner's statement that Mardon anticipates claim 38 is erroneous and in direct contrast with the Examiner's previous admission that Mardon does not disclose or suggest all of the elements of claim 38. *See* the June 21, 2005 final Office Action at sections 7 and 6, respectively. The Examiner's refusal to consider the declaration of Magnus Limbäck, which was submitted with the Response to the January 28, 2005 non-final Office Action and attached here as Exhibit A, is improper. The Examiner must consider the declaration.

The declaration, together with the other previously filed declaration (attached here as Exhibit B), is in fact highly relevant to the non-obviousness of the present invention. From the declarations it is clear that the present invention provides unexpected and advantageous results.

Thus, the Examiner's rejections of claim 38 is improper and must be withdrawn.

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Rejections of Claims 22, 23, 36, and 37 under 35 U.S.C. § 103 over Mardon modified by Van Swam

Claims 22 and 36 require an inner circumference of the cladding tube to be provided with a layer of material that is more ductile than the cladding tube alloy, while claims 23 and 37 limit the amount of alloying elements. In the newly added rejections of these claims, the Examiner proffers a combination of Mardon modified by Van Swam. The Examiner has equated the outer layer of Mardon with the cladding tube defined in instant claims 13 and 35, from which claims 22, 23, 36, and 37 ultimately depend. Mardon explicitly teaches an inner layer (in fact, the main layer in the cladding tube of Mardon) that is provided on the inner circumference of the outer layer of Mardon. This inner layer in Mardon is not the same kind of layer as the inner layer in the three-layer structure of Van Swam to which the Examiner now refers. As previously explained, there is no indication that the inner layer of Mardon is more ductile than the outer layer. Furthermore, it would not be obvious to change the composition of the inner layer of Mardon in view of Van Swam. In fact, Van Swam describes a typical duplex tube as prior art. *See* Van Swam at column 2, lines 22-31. The prior art tube there described is similar to the cladding tube of Mardon. Van Swam teaches the use of different alloys in order to overcome the disadvantages of the prior art. In order to overcome these disadvantages, Van Swam teaches particular alloy structures with two or three layers in the tube. It is thus clear that Van Swam teaches away from the prior art as exemplified in, for example, Mardon. Consequently, it would not be obvious to apply a layer as described in the specific context of Van Swam to the prior art cladding tube of Mardon. Instead, Van Swam explicitly teaches a combination of layers of different compositions that should be used instead of the traditional duplex layers like those disclosed in Mardon.

Furthermore, in rejecting the independent claims from which claims 22, 23, 36, and 37 ultimately depend, the Examiner relied upon the disclosure of Mardon defining the composition of the inner layer of its tube. The Examiner then attempts to re-define the very same composition to be something different when addressing the dependent claims. The Examiner cannot assign such contrasting definitions to a single term. In doing so, the Examiner has removed the definition of the composition of the cladding tube, and thus the Examiner has not addressed each of the claim elements.

Thus, in addition to being allowable due to their dependence from allowable independent claims, claims 22, 23, 36, and 37 are further allowable because the Examiner's rejections of these claims are improper and must be withdrawn.

Rejection of Claims 39 and 40 under 35 U.S.C. § 103 over Mardon modified by Garde '774 and Van Swam

The comments presented immediately above with respect to claims 22, 23, 36, and 37 apply equally to claims 39 and 40, and are incorporated herein. The Examiner's further inclusion of Garde '774 here further establishes the Examiner's rejections as being improper and too far-reaching.

Suffice it to say that Mardon describes one kind of traditional duplex tube. Van Swam explicitly teaches alternatives that should be used *instead of* a traditional duplex tube, and in the embodiment cited by the Examiner, a three-layer tube. Van Swam therefore cannot properly be combined with Mardon as proffered by the Examiner. Additionally, Garde '774 clearly teaches away from Mardon as previously discussed herein.

CLAIMS APPENDIX

1 13. A cladding tube for nuclear fuel, the cladding tube being made of a zirconium-based

2 alloy suitable for use in a corrosive environment where it is subjected to increased radiation, the

3 alloy having a quality and impurity level, including up to 1600 ppm O and up to 120 ppm Si,

4 suitable for use in nuclear reactors, the alloy consisting essentially of:

5   0.65-1.6 percent by weight Nb;

6   0.3-0.6 percent by weight Fe;

7   0.65-0.85 percent by weight Sn; and

8   the balance being Zr.

1 22. The cladding tube according to claim 13, wherein at least a part of an inner circumference

2 of the cladding tube is provided with a layer of a material that is more ductile than the alloy.

1 23. The cladding tube according to claim 22, wherein the layer comprises a zirconium-based

2 alloy having a total content of alloying elements that does not exceed 0.5 percent by weight.

1 35. A cladding tube for nuclear fuel, the cladding tube being made of a zirconium-based

2 alloy suitable for use in a corrosive environment where it is subjected to increased radiation, the

3 alloy having a quality and impurity level, including, optionally, 500-1600 ppm O and, optionally,

4 50-120 ppm Si, suitable for use in nuclear reactors, the alloy consisting essentially of:

5   0.65-1.6 percent by weight Nb;

6   0.3-0.6 percent by weight Fe;

7   0.65-0.85 percent by weight Sn; and

8   the balance being Zr.

1   36.   The cladding tube according to claim 35, wherein at least a part of an inner circumference

2   of the cladding tube is provided with a layer of a material that is more ductile than the alloy.

1   37.   The cladding tube according to claim 36, wherein the layer comprises a zirconium-based

2   alloy having a total content of alloying elements that does not exceed 0.5 percent by weight.

1   38.   A cladding tube for nuclear fuel, the cladding tube being made of a zirconium-based

2   alloy suitable for use in a corrosive environment where it is subjected to increased radiation, the

3   alloy having a quality and impurity level, including 500-1600 ppm O and 50-120 ppm Si,

4   suitable for use in nuclear reactors, the alloy consisting essentially of:

5   0.65-1.6 percent by weight Nb;

6   0.3-0.6 percent by weight Fe;

7   0.65-0.85 percent by weight Sn; and

8   the balance being Zr.

1   39.   The cladding tube according to claim 38, wherein at least a part of an inner circumference

2   of the cladding tube is provided with a layer of a material that is more ductile than the alloy.

1   40.   The cladding tube according to claim 39, wherein the layer comprises a zirconium-based

2   alloy having a total content of alloying elements that does not exceed 0.5 percent by weight.

EVIDENCE APPENDIX

1.   A copy of the declaration of Magnus Limbäck, which was submitted with the Response

to the January 28, 2005 non-final Office Action, is attached hereto as Exhibit A.

2.   A copy of the declaration of Magnus Limbäck, which was submitted with the Response

to the December 24, 2003 non-final Office Action, is attached hereto as Exhibit B.

3.   A new declaration of Magnus Limbäck is attached hereto as Exhibit C.

RELATED PROCEEDINGS APPENDIX

None.

CONCLUSION

In view of the foregoing arguments, the Appellants respectfully request reconsideration and withdrawal of the claim rejections, and that the application be passed to issuance. Failing that, the Appellants respectfully request the Board to overrule the Examiner's rejections, based on the explanations presented above, and to pass this application to issuance.

As the appeal brief fee set forth in 37 CFR 41.20(b)(2) has already been filed in conjunction with the Appeal Brief filed on December 14, 2005 and this Substitute Appeal Brief was filed in response to the Examiner's deletion of claim rejections issued in the final Office Action and inclusion of newly presented claim rejections first issued in the Examiner's Answer, no further appeal brief fee is believed due. However, should the Commissioner deem otherwise, the Commissioner is hereby authorized to charge such an additional appeal brief fee and any insufficiency or credit any overpayment associated with this application to Bingham McCutchen LLP Deposit Account No. 19-5127 (order no. 19378.0011).

Respectfully Submitted,

Dated: April 14, 2006

Sean P. O'Hanlon
Reg. No. 47,252

Bingham McCutchen LLP
3000 K Street, NW
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Washington, DC 20007
(202) 295-8429

DECLARATION

I, Magnus Limbäck, M.Sc. in Engineering Physics, employed at Westinghouse Electric Sweden AB and there responsible for BWR fuel material, make the following declaration.

I.

I have previously made a declaration, signed by me on 22 June 2004, in this case.

I have now noticed that the declaration contains typing errors in connection with Figure 3. These errors are that the same alloy (Zr1.5Nb0.5Sn0.3Fe) has been entered twice in the legend to the right of the figure and twice in the rectangles pointing to the figure itself.

I here below, on the next page, enclose a corrected Figure 3. The places where the figure has been corrected are marked by arrows pointing to the corrected entries.

When further below in this declaration Figure 3 is mentioned, it is being referred to the corrected Figure 3. When Figures 1 and 2 are mentioned, it is being referred to these Figures in the previous declaration.
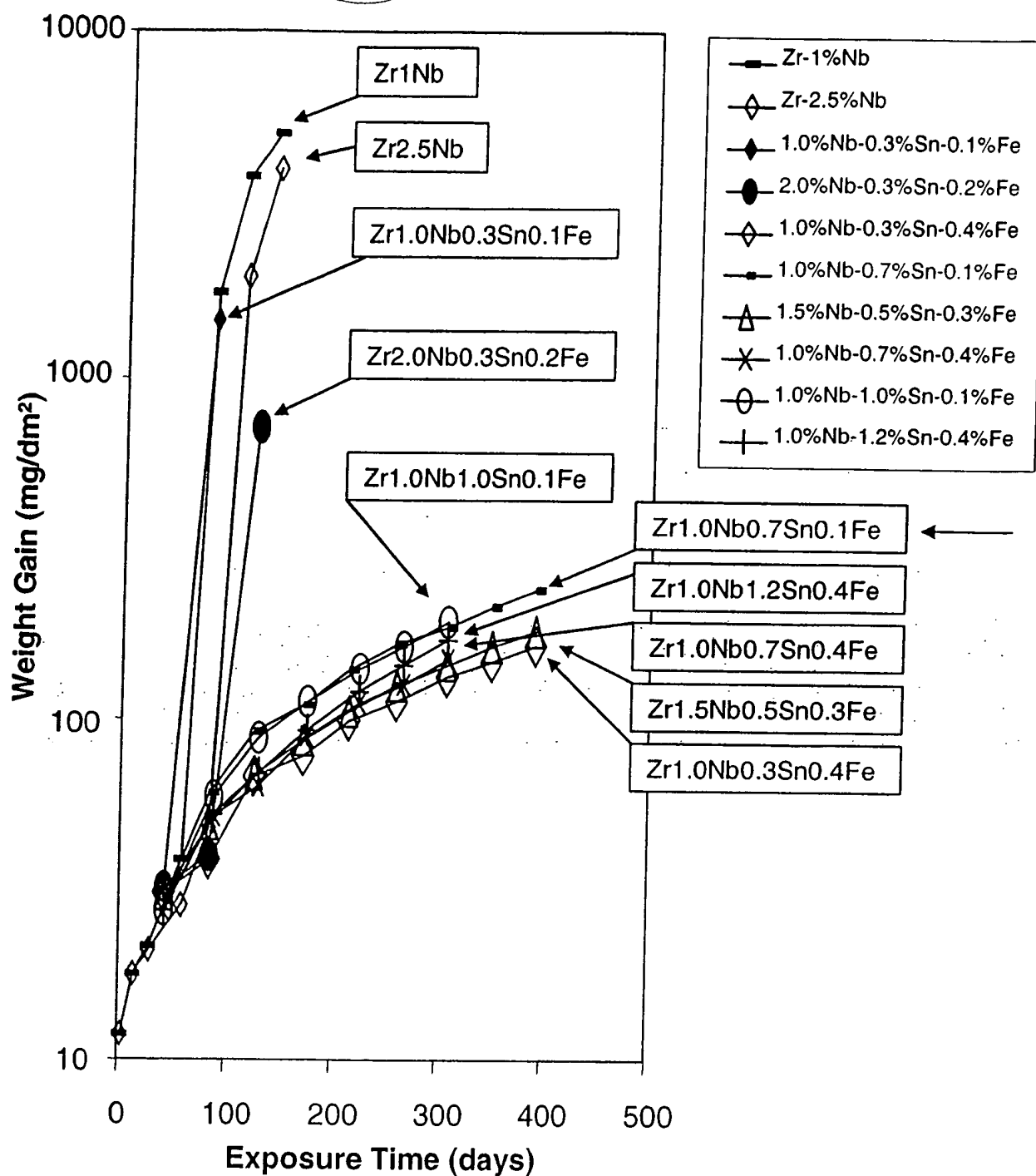
Figure 3: Long term corrosion test of coupons in 70 ppm lithiated water at 633 K.

II.

In addition to the to the statements made above, and in the previous declaration, I hereby add the following.

The results from the 633 K pure water (Fig. 2) and the 700 K steam (Fig. 1) tests indicate that the Sn concentration should be as low as possible within the studied interval to optimize the corrosion resistance in these environments. On the other hand, Fig. 3, which presents the results from the 633 K 70 ppm lithiated water tests, shows two classes of materials, one that is sensitive to Li-induced acceleration of the corrosion rate and one that is almost immune against this type of acceleration. For the inventors of the product described in the current patent application it has been important to assure that the newly developed material will belong to the second improved group.

It is, thus, of special interest to compare the results for four of the materials included in Fig. 3, Zr1.0Nb0.3Sn0.1Fe, Zr1.0Nb0.7Sn0.1Fe, Zr1.0Nb0.3Sn0.4Fe and Zr1.0Nb0.7Sn0.4Fe. The first of these four materials experiences Li-induced acceleration of the corrosion rate, while the latter three have very good resistance against such acceleration. It is concluded that the difference in performance between these alloys is due to the difference in chemical composition. The alloy with poor corrosion resistance has low Sn (0.3 wt%) and low Fe (0.1 wt%) contents, while the alloys with very good resistance have higher Sn (0.7 wt%) and/or higher Fe (0.4 wt%) concentrations. The data, consequently, shows that the corrosion resistance is improved by increasing the Sn concentration from 0.3 to 0.7 wt% and by increasing the Fe content from 0.1 to 0.4 wt%.

The effect of Sn and Fe concentration on the corrosion performance is further elucidated by plotting subsets of the data presented in Fig. 3. Figure A, consequently, depicts the weight gain measured after 84 days as a function of Sn concentration for Zr1.0NbxSn0.1Fe type materials. This graph shows the significant improvement in corrosion resistance that is gained by increasing the Sn content from 0.3 to 0.7 wt%. Figure B, furthermore, shows the beneficial effect of increasing the Fe concentration in Zr1.0Nb0.7SnxFe type materials that is observed after 307 days.
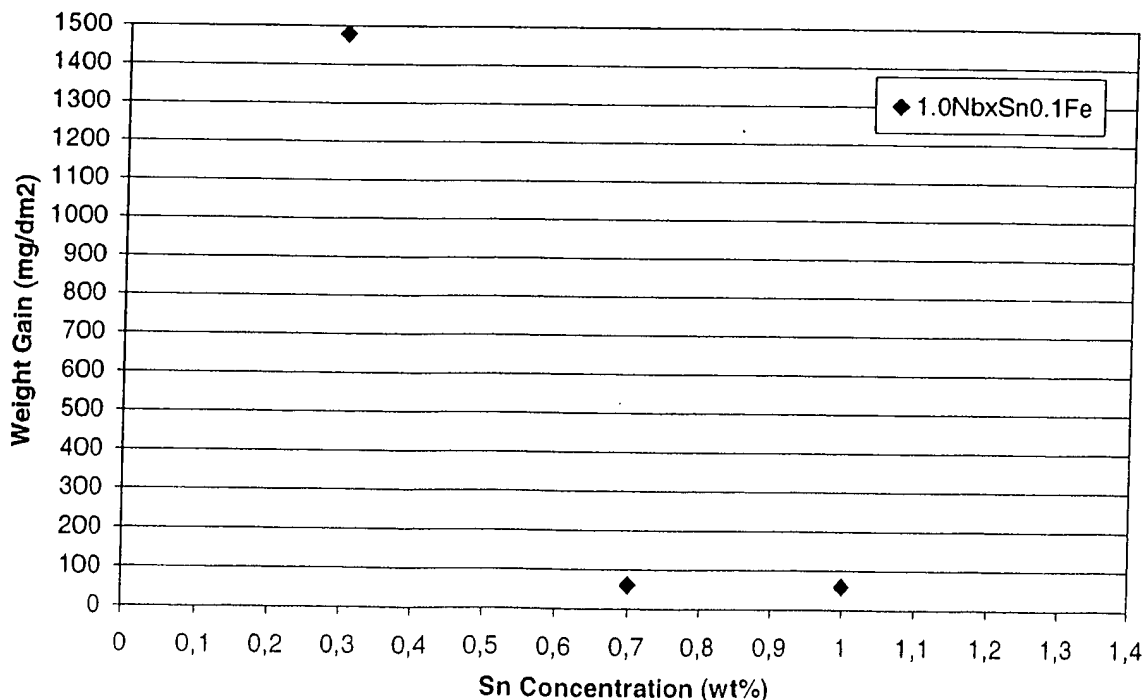

Figure A: Weight gain as a function of Sn content for Zr1.0NbxSn0.1Fe type materials after 84 days exposure at 633 K in 70 ppm lithiated water.
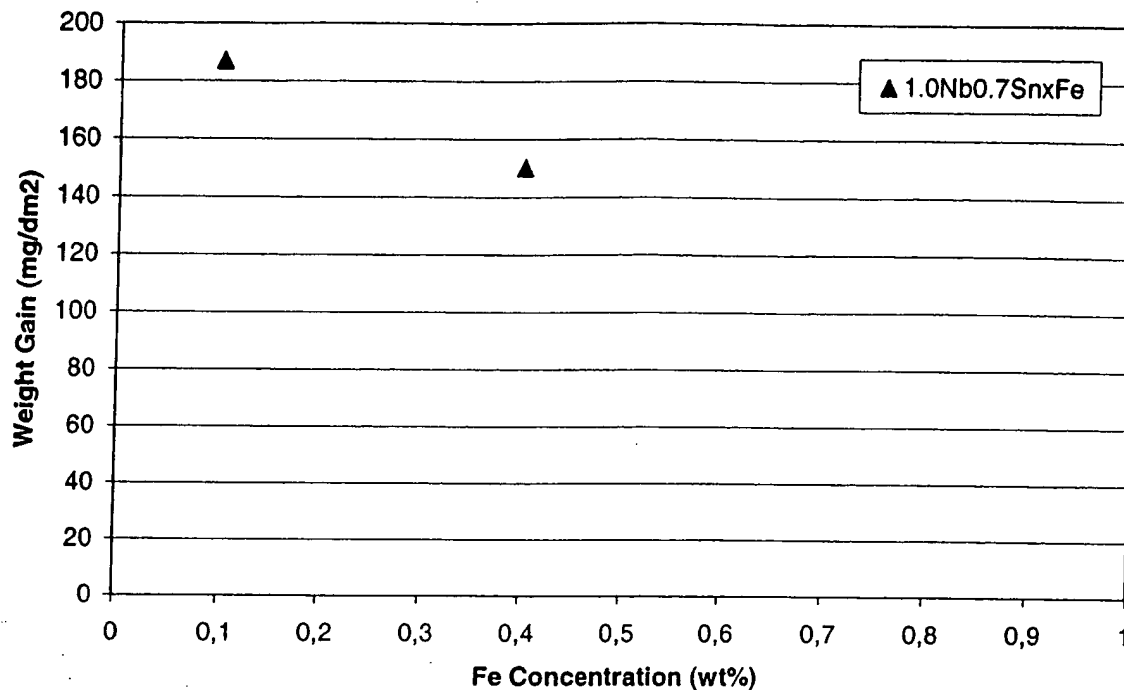
Figure B: Weight gain as a function of Fe content for Zr1.0Nb0.7SnxFe type materials after 307 days exposure at 633 K in 70 ppm lithiated water.

The goal of the current development is an alloy that is robust and has very good corrosion resistance not only in autoclaves but also, and more importantly, in various types of in-reactor environments. The inventors have applied a redundant approach where the two improving factors, i.e., increased Fe and Sn concentrations, are combined. The inventors have, consequently, chosen an alloy with >0.65 wt% Sn in combination with >0.30 wt% Fe.

In addition to the test results presented earlier a corrosion test has also been made in steam at 415°C (688 K). The results are presented in Fig. C and show that decreasing the Sn content from 1.14 to 0.95 drastically improves the corrosion resistance. The data, moreover, show that decreasing the Sn content to 0.8 wt% further improves the corrosion resistance, but that the material with 0.65 wt% Sn has about the same corrosion resistance as the material with 0.8 wt% Sn. These observations are all valid for materials with 0.32-0.35 wt% Fe. When comparing the two materials with 0.65-0.67 wt% Sn it can be observed that the material with the higher Fe content (0.35 wt%) has somewhat better corrosion resistance than the material with lower Fe concentration (0.10 wt%).
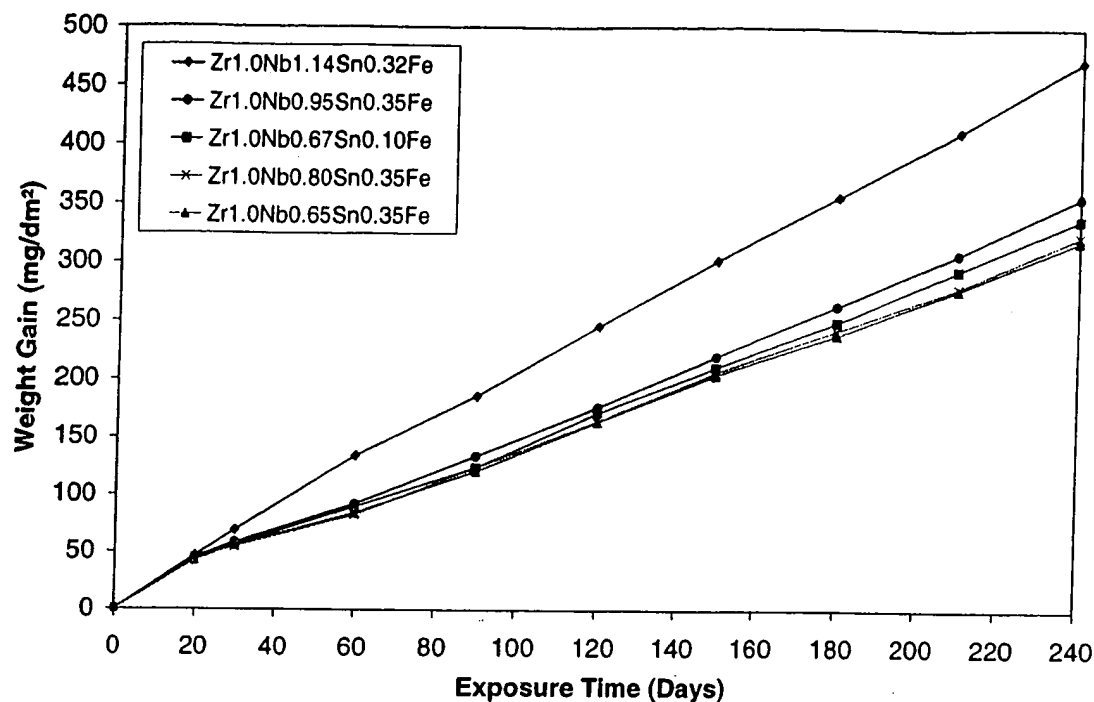
Figure C: Long term autoclave test results of coupons in steam at 688 K.

Based on the results from the 633 K 70 ppm lithiated water, 633 K pure water and 700 K steam tests presented earlier along with the 688 K steam test presented here, the inventors conclude that the Sn concentration should be within a rather narrow region, 0.65-0.85 wt%. The inventors, further, conclude that the Fe concentration should be 0.3-0.6 wt%, where the lower limit is chosen to secure good corrosion resistance while the upper limit is chosen to minimize potential fabrication issues, i.e., secure a good production yield.

I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Västerås, Sweden, 26 April 2005

Magnus Limbäck

DECLARATION

Re: US patent application 09/857606

I, Magnus Limbäck, M.Sc. in Engineering Physics, employed at Westinghouse Electric Sweden AB and there responsible for BWR fuel material, make the following declaration concerning tests made of alloys for use in nuclear energy plants.

The tests were performed by Westinghouse Electric Corporation, USA, in cooperation with Westinghouse Electric Sweden AB.

The corrosion performance of alloys of the type ZrxNbySnzFe (Zr alloy with x, y and z wt% Nb, Sn and Fe, respectively.) in different environments has very recently been presented by one of the inventors behind the current patent application along with five co-authors [1]. The studied material types are presented in Table 1.

The corrosion performance was evaluated by autoclave tests that were conducted in a manner consistent with ASTM Practice for Aqueous Corrosion Testing of Samples of Zirconium and Zirconium Alloys (G2). Exposures in 633 K water were performed at saturation pressure while exposures at 700 K steam were performed at 10.3 MPa. Testing at 633 K included both pure water and lithiated water containing 70 ppm Li that was added as lithium hydroxide. The autoclave tests were periodically interrupted to obtain corrosion weight gains of the specimens. Testing included three specimens per alloy, and the reported corrosion data represent the average specimen weight gains. The corrosion test results in steam at 700 K, pure water at 633 K and 70 ppm lithiated water at 633K are depicted in Figs. 1-3, respectively.

The corrosion behavior in steam at 700 K and pure water at 633 K was quantified by calculating the post transition corrosion rate for each alloy composition by performing a linear least squares fit of the data. The rates were calculated over the time interval of 140 to 469 days for 633 K water and 61 to 251 days for 700 K steam. Also included for comparisons in the corrosion evaluations are results from two Zr-Nb binary alloy samples that were previously reported [2].

The effect of chemistry on corrosion behavior was examined by assessing the impact of the chemistry variations on corrosion rates. Corrosion rates were plotted as a function of individual alloying elements in order to identify potential relationships between alloy chemistry and corrosion behavior. Figure 4 shows the relationship between normalized corrosion rates in 633 K water and 700 K steam as a function of three chemistry variables (Nb, Sn, and Fe). The rates were normalized relative to those of an alloy with a nominal chemistry of Zr-1Nb-1Sn-0.1Fe.

Figure 4a shows the impact of tin on the corrosion rate. Even with variations of other alloying elements, the impact of tin on the corrosion rate in the two environments is apparent. In both pure water and steam environments, the corrosion rate decreases with decreasing tin content. The rate of change in the autoclave tests is about a 5% decrease in corrosion rate for each 0.1% decrease in tin. Figures 4b and 4c show the relative corrosion rates plotted as functions of the niobium and iron contents, respectively. Figure 4b shows that there is no significant correlation with niobium variations. Likewise Figure 4c shows that the effects of variation in iron content on corrosion rates in these environments are secondary in comparison to the tin effects.

Figure 3 is a plot of corrosion weight gains of the various alloys in 70 ppm lithiated water at 633K. In the lithiated water environment, the corrosion rate is only slightly affected by the tin content until it is below a threshold tin value. This suggests that a minimum critical tin content is needed to prevent accelerated corrosion in the lithiated water environment. While the tin content was not studied as an entirely independent variable, non-linear multiple regression analysis was utilized to evaluate the impact of the main alloying elements on the uniform corrosion rate in lithiated water. The result of this analysis indicates that tin is clearly an important factor in the resistance to accelerated corrosion in high lithium environments.

In addition to the beneficial impact of tin on the uniform corrosion rate in the lithiated environment, there is also indication that iron may provide a similar effect. A comparison of two alloys, Zr1.0Nb0.3Sn0.1Fe and Zr1.0Nb0.3Sn0.4Fe, shows iron also contribute to the delay of the accelerated corrosion in high lithium environment. Figure 5 is a plot of relative corrosion rates in 70 ppm lithiated water as a function of the combined iron and tin levels. The results indicate that a combination tin and iron in the alloy provides resistance to accelerated corrosion from 70 ppm lithiated water autoclave tests. It was suspected that the individual effects of tin and iron on lithium accelerated corrosion are not totally equivalent but the initial comparison as shown in Figure 5 indicates the effects of both tin and iron.

In-reactor corrosion is a complex phenomenon and the 70 ppm Li environment is used to simulate the Li accelerated corrosion that might occur in the upper spans of high power fuel assemblies, which may experience concentrated lithium conditions in the oxide due to sub-cooled boiling at the cladding surface. A second possible Li concentration mechanism is boiling in crud on the rod surface. With recent utilities' desire to operate at higher coolant lithium concentrations to control coolant pH and reduce crud formation, lithium corrosion resistant alloys are an important part of robust fuel designs.

It is, finally, concluded that the results from the various tests and analyses strongly support the invention described in the current patent application. The proposed chemical composition provides a material with very good corrosion resistance in all of the studied environments. In addition, the presence of tin at a well optimized level, as the one put forward in the patent application, helps to maintain good mechanical strength, primarily creep and tensile strengths.

Table 1: Nominal alloy chemistry.

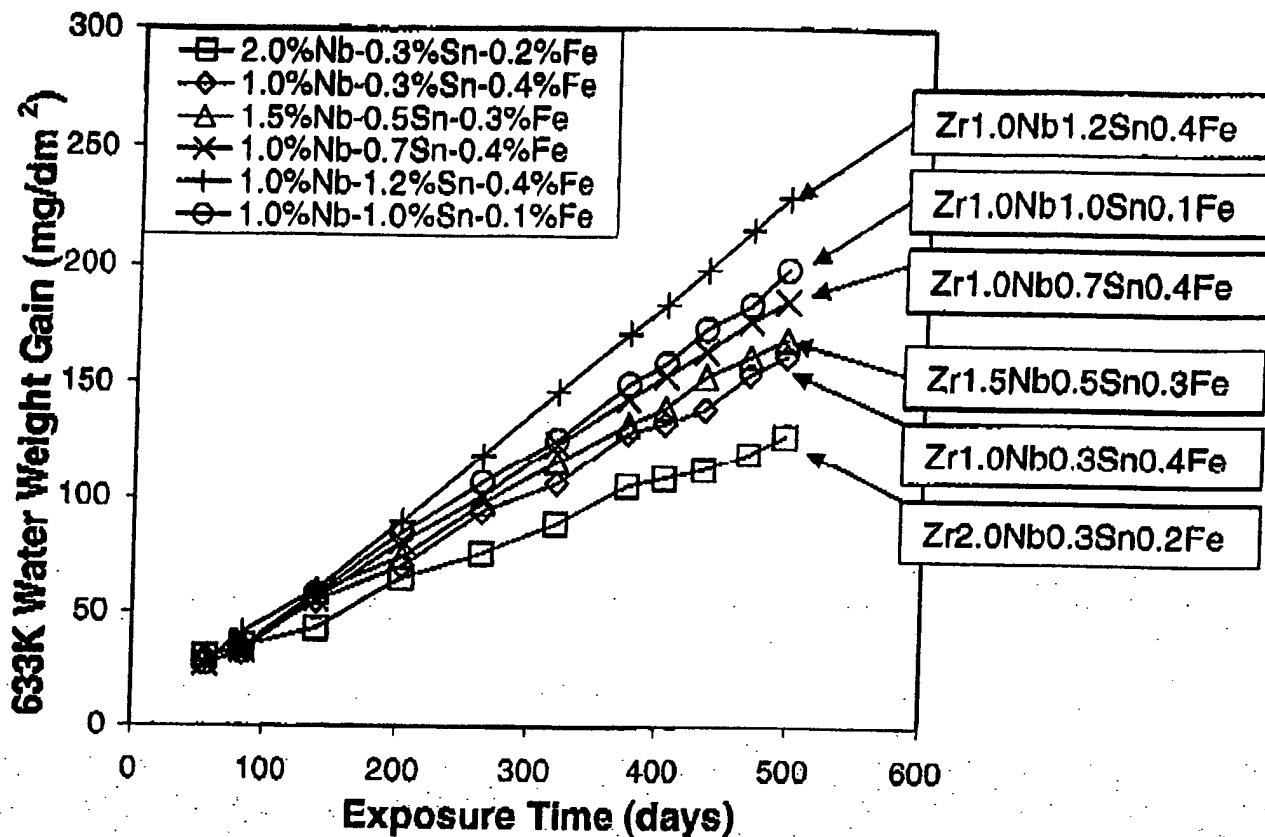| Alloy ID	Alloy Elements Composition (wt%)		
	Nb	Sn	Fe
Group 1 (variable tin)			
1-1	1.0	1.3	0.1
1-2	1.0	1.0	0.1
1-3	1.0	0.7	0.1
1-4	1.0	0.3	0.1
Group 2 (high iron, variable tin)			
2-1	1.0	1.2	0.4
2-2	1.0	0.7	0.4
2-3	1.0	0.3	0.4
Group 3 (high niobium, high iron, low tin)			
3-1	1.5	0.5	0.3
3-2	2.0	0.3	0.2

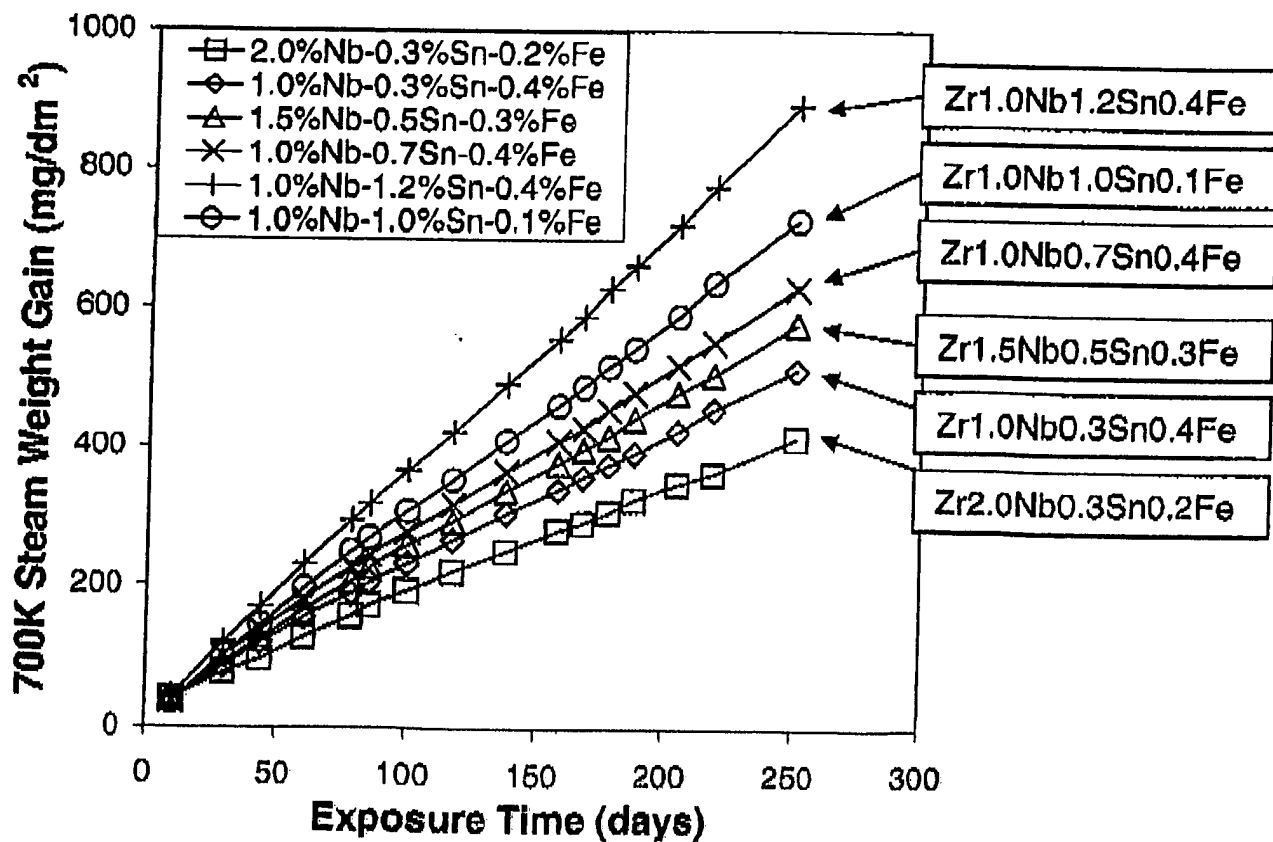Figure 1: Long term autoclave test results of coupons in steam at 700 K.

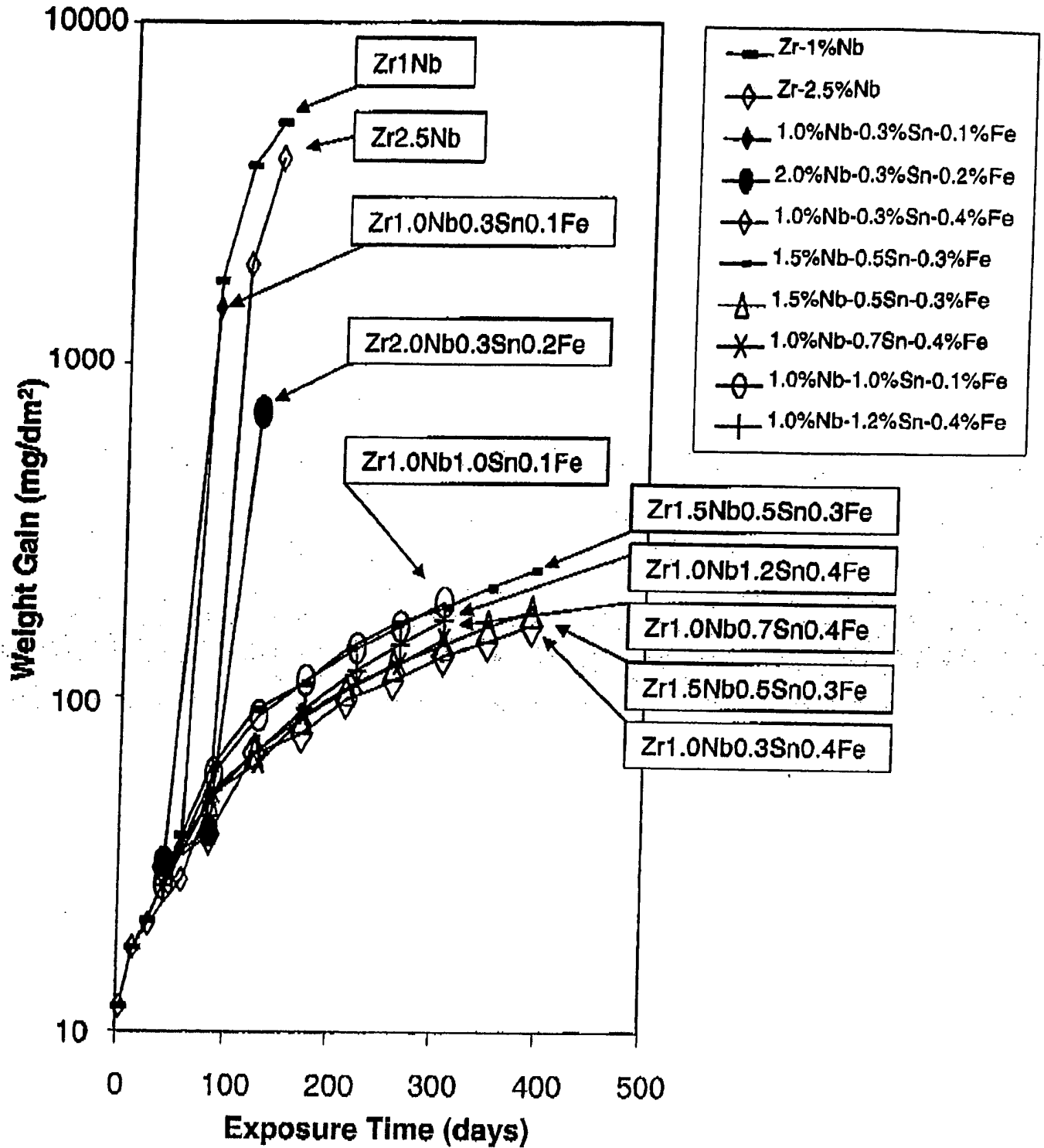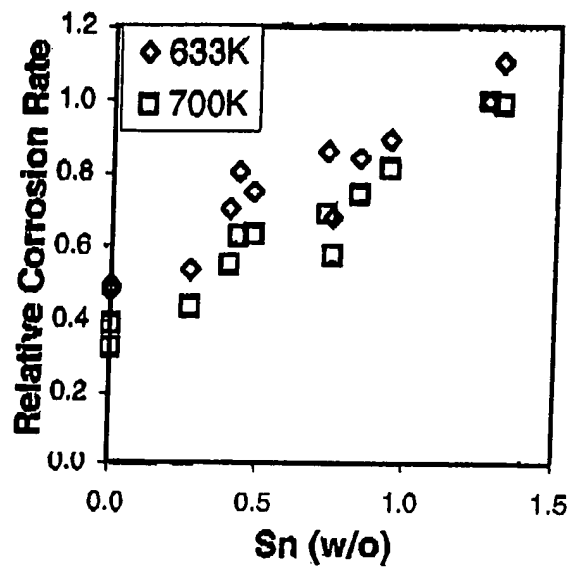Figure 2: Long term autoclave test results of coupons in pure water at 633 K.
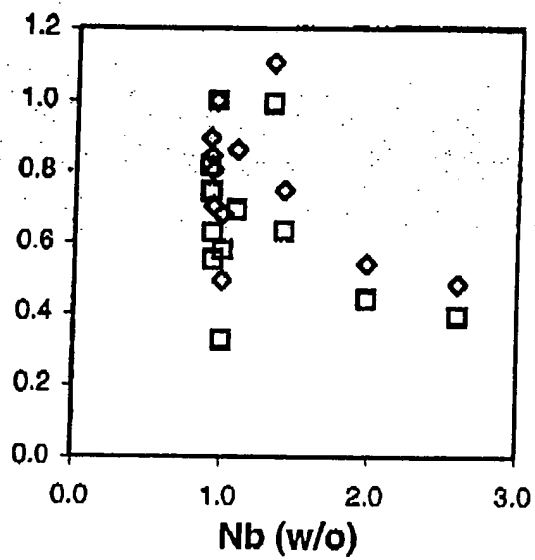
Figure 3: Long term autoclave test results of coupons in 70 ppm lithiated water at 633 K.
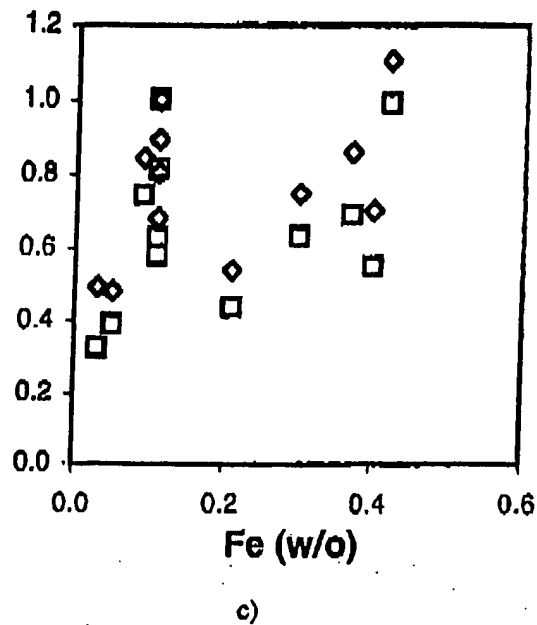
a)

b)

c)

Figure 4: Variation in normalized (to 1%Sn-1%Nb-0.1%Fe) corrosion rate as a function of chemistry variable: a) tin, b) niobium, and c) iron.
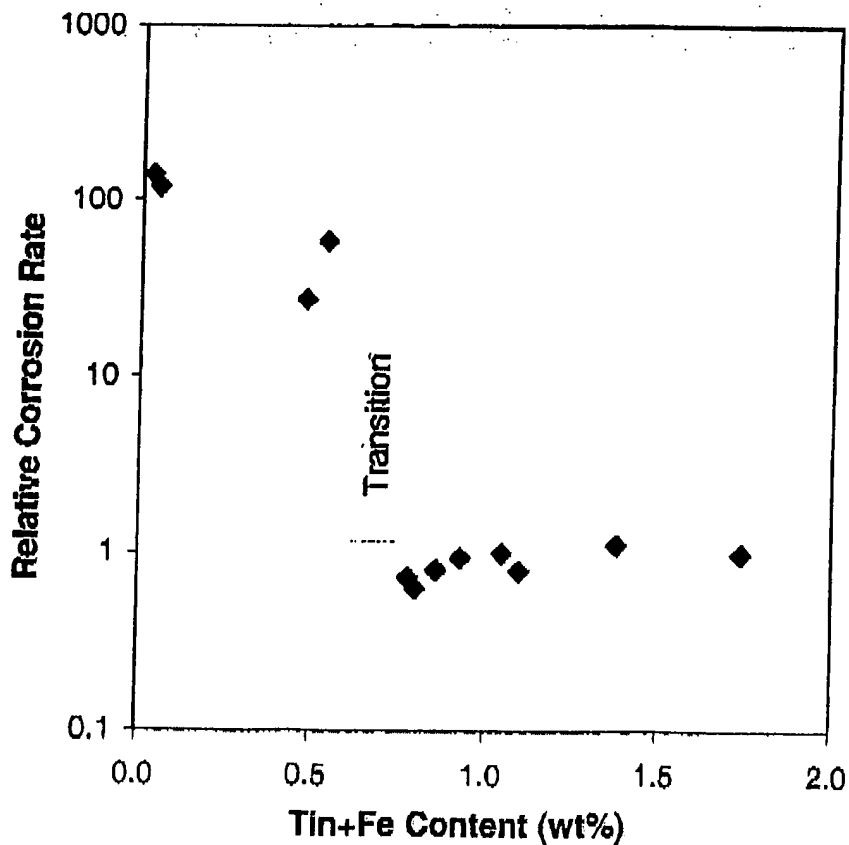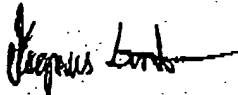

Figure 5: Impact of tin and iron content on corrosion rate in 633K-70 ppm lithiated water environment.

References

[1]   H.K. Yueh, R.L. Kesterson, R.J. Comstock, D.J. Colburn, M. Dahlbäck and L. Hallstadius, "Improved ZIRLO^{TM} Cladding Performance through Chemistry and Process Modifications". Paper presented at the ASTM 14th International Symposium on Zirconium in the Nuclear Industry, Stockholm, Sweden, June 13-17, 2004.

[2]   R.J. Comstock, G. Schoenberger and G.P. Sabol, "Influence of Processing Variables and Alloy Chemistry on the Corrosion Behavior of ZIRLO Nuclear Fuel Cladding", ASTM STP 1295, 1996, P710.

I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Västerås, Sweden, 22 June 2004

Magnus Limbäck

DECLARATION

Re: US patent application 09/857606

I, Magnus Limbäck, M.Sc. in Engineering Physics, employed at Westinghouse Electric Sweden AB and there responsible for BWR fuel material, make the following declaration, in addition to the previously filed declarations concerning this case.

The effect of Si on hydrogen pickup

After the publication of the patent of Garde et al. (US 5,211,774) it was found that the effect of Si on hydrogen pickup is observed in Ni-bearing Zr-based alloys, e.g., Zircaloy-2, but not in Zr-based alloys that do not include Ni as an alloying element, e.g., Zircaloy-4 [1]. It is concluded that additions of silicon decreases the negative effect of nickel on the hydriding properties of Zircaloy-2 [1]. Since Ni is not used as an alloying element in the invention put forward in the current patent application, Si is not added to reduce the hydrogen pickup.

Multi-Layer Claddings

Today two types of multi-layer claddings are used commercially in nuclear fuel. The two claddings are developed to improve the performance in different aspects. A thin inner layer, a liner, is used to improve the resistance against Pellet-Cladding Interaction (PCI) failures, while a thin outer layer, so called Duplex tubing, is used to improve the corrosion resistance of the outer surface. In both cases, i.e., both for liner (inner layer) and Duplex (outer layer) claddings, the thin layer is normally about 10% of the wall thickness.

In both cases the material used for the thin outer or inner layers has limitations that impede the use of these types of materials as the main component of the tubing. The considered materials have rather poor mechanical strength and do for example not provide the creep resistance needed for the use as the main component of nuclear fuel cladding. The reason for the poor mechanical strength is the low concentration of alloying elements.

Westinghouse has in cooperation with Sandvik Materials Technology (SMT) performed a multitude of creep tests. The procedure used when testing the creep properties are presented in [2] along with a subset of the test data covering various types of Zircaloy-2 and Zircaloy-4 claddings. Apart from these types of materials, single component cladding tubes fabricated from so called dilute Zr-based alloys, i.e., alloys with low concentrations of alloying elements, and ZrSnNbFe alloys have also been creep tested. The considered dilute alloys have chemical compositions similar to those normally used for the outer component in Duplex types cladding, which in turn includes a higher concentration of alloying elements than a typical (inner) liner

material. The data elucidate limitations of these types of dilute alloys, which do not provide a creep strength that is adequate for use as single component cladding tube in a nuclear reactor. Table 1 presents the chemical composition of the dilute alloys along with reference Zircaloy-2 and Zircaloy-4 materials as well as ZrSnNbFe alloys covered by the current patent application (alloys with Lot No 81270 and 81271), while Table 2 presents creep data for the considered materials.

It can be observed that the creep rate is a factor of 6-10 higher for the dilute alloys as compared to the Zircaloy-2 and Zircaloy-4 materials. This large difference in mechanical properties is the explanation behind the two-component tubing concepts used in liner and Duplex claddings. As mentioned above, these cladding types have either a thin inner (liner) or outer (Duplex) layer of a dilute alloy, while the main component consists of a Zr-based material with good mechanical properties, such as Zircaloy-2, Zircaloy-4 or the type of alloy put forward in the current patent application.

From Table 2, it can furthermore be observed that the creep strength of the ZrSnNbFe type alloys covered by the current patent application is similar to the creep strength of Zircaloy-2 and Zircaloy-4 materials.

Table 1: *Chemical compositions.*

Lot No	Material Type	Weight Percent						ppm		
		Sn	Fe	Cr	Ni	V	Nb	Si	O	C
81408	Zircaloy-4	1.34	0.20	0.10	-	-	-	80	1340	135
81410	Dilute	0.009	0.28	0.003	-	0.25	-	120	2220	150
81411	Dilute	0.27	0.27	0.002	-	-	-	60	1590	130
81415	Dilute	0.52	0.4	-	-	-	-	92	1243	139
81416	Zircaloy-2	1.36	0.16	0.10	0.05	-	-	75	1295	130
81270	ZrSnNbFe	0.68	0.33	-	-	-	0.94	50	1045	30
81271	ZrSnNbFe	0.76	0.36	-	-	-	0.96	50	995	35

Table 2: *Measured Creep Strains for a Hoop Stress of 120 MPa at 385°C.*

Lot No	Material Type	Creep Strain in % after			
		120 h	240 h	360 h	480 h
81408	Zircaloy-4	0.55	0.80	1.04	1.22
81410	Dilute	2.58	4.31	6.09	7.79
81411	Dilute	2.86	4.76	6.65	8.52
81415	Dilute	3.21	5.66	8.69	12.11
81416	Zircaloy-2	0.52	0.76	0.94	1.17
81270	ZrSnNbFe	0.48	0.80	1.12	1.42
81271	ZrSnNbFe	0.50	0.79	1.06	1.34

Duplex tubing

Mardon et al. (US 5,023,048) proposes a Duplex tubing with an outer layer of a ZrSnFe(Nb)(V) alloy and an inner component made of Zircaloy-2, Zircaloy-4 or Zr-1wt%Nb. The Sn concentration in the outer layer is proposed to be 0.35-0.65 wt%. The same range is proposed also for the Nb content.
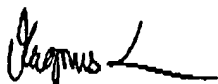
The invention presented in our patent application proposes higher Sn and Nb concentrations than what is proposed by Mardon et al. The chemical composition proposed in our application is chosen since it provides many advantages, one is improved corrosion resistance discussed in an earlier declaration, and a second is improved mechanical strength. The data presented in Table 2, above, clearly show the benefit for the mechanical properties when increasing the concentration of alloying elements. One of the main advantages of our invention, consequently, is that the proposed alloy provides very good mechanical properties, in combination with excellent corrosion resistance, and thus can be used as the main component of a cladding tube, not only as a thin corrosion resistant outer layer as proposed by Mardon et al. for the alloy put forward in US 5,023,048.

References

[1] M. Limbäck, M.A. Krammen, P. Rudling, S.R. Pati, and A.M. Garde, "Corrosion and Hydriding Performance of Zircaloy-2 and Zircaloy-4 Cladding Materials in PWRs",
Paper presented at the American Nuclear Society 1994 International Topical Meeting on Light Water Reactor Fuel Performance, West Palm Beach, Florida, April 17 - 20, 1994.

[2] M. Limbäck and T. Andersson, "A Model for Analysis of the Effect of Final Annealing on the In- and Out-of-Reactor Creep Behavior of Zircaloy Cladding",
Zirconium in the Nuclear Industry: 11th International Symposium, ASTM STP 1295, 1996, pp. 448-468.

I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such wilful false statements may jeopardise the validity of the application or any patent issuing thereon.

Västerås, Sweden, 29 March 2006

Magnus Limbäck